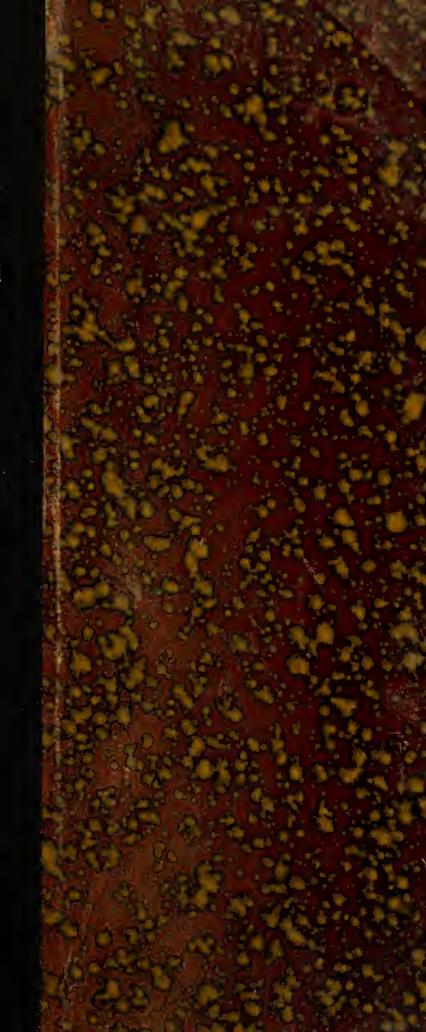# SEESE

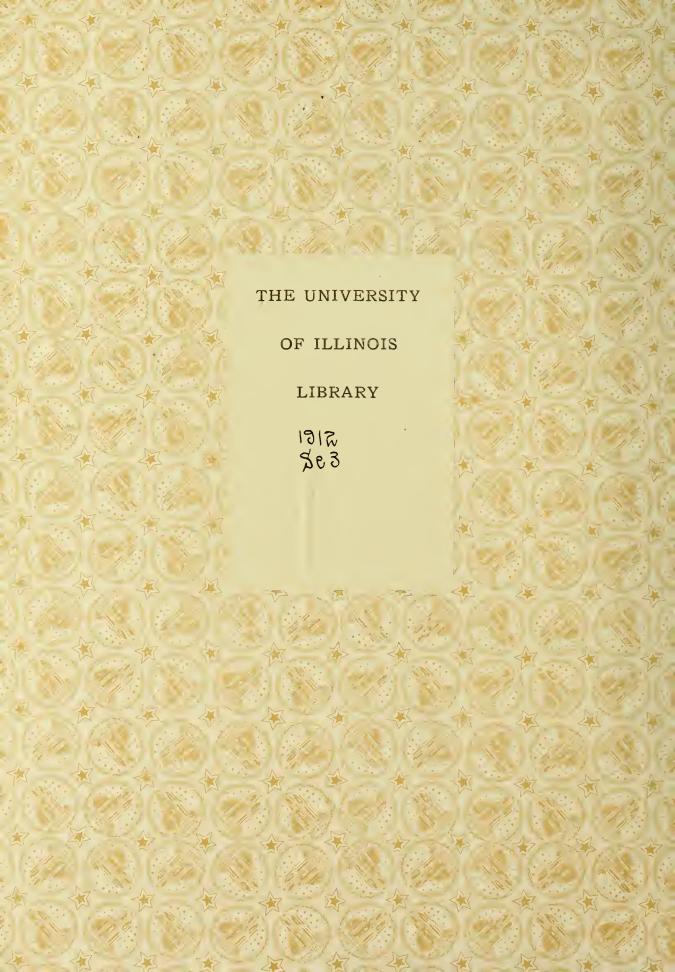# Investigation of the Aluminium Cell

Electrical Engineering

B. S.

1912

INVESTIGATION OF THE ALUMINIUM CELL

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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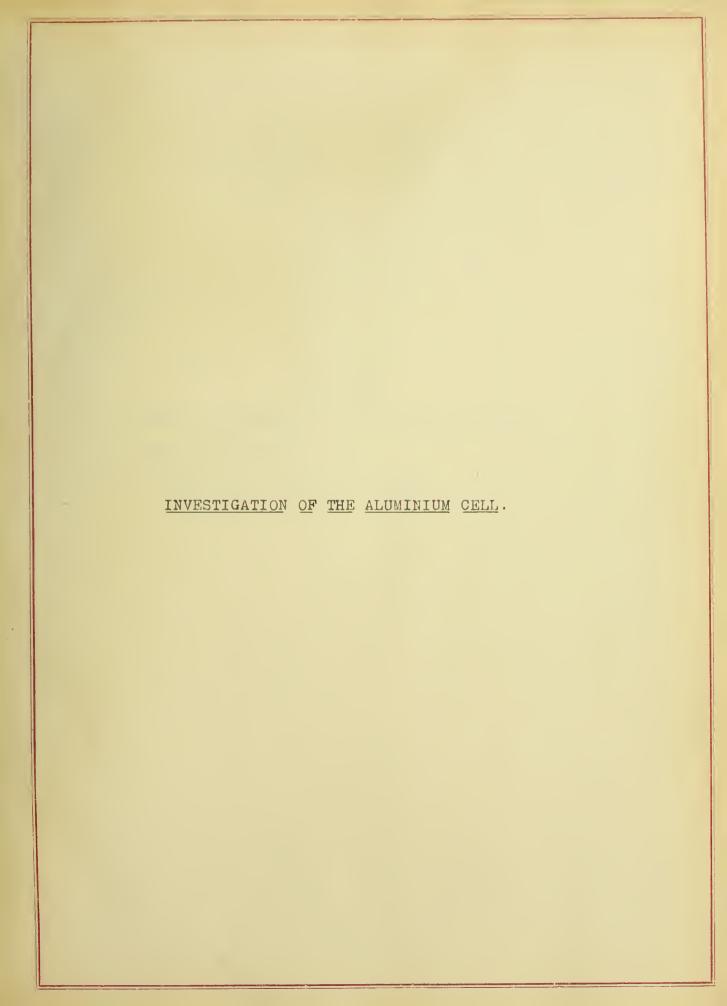
ENTITLED INVESTIGATION OF THE ALUMINIUM CELL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN ELECTRICAL ENGINEERING

Instructor in Charge

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HEAD OF DEPARTMENT OF ELECTRICAL ENGINEERING.

INVESTIGATION OF THE ALUMINIUM CELL.

CONTENTS.

INTRODUCTION.

The development of the aluminium cell has proceeded slowly for two reasons: the general distrust of electrochemical apparatus when replacing mechanical devices, and the fact that as yet very little is known regarding the cell. There is, however, a considerable demand for a device having some of the properties of the cell, and it is probable that in the future some further improvements may render it a valuable asset to the electrical industries.

It is the purpose of this paper to point out some of the principal characteristics of the cell, as well as to describe its several applications to electrical engineering work. Thorough investigation into the many problems connected with it is necessarily limited, but it is hoped to make this the basis of some future work.

CHAPTER ONE.

General Characteristics.

The principal feature of an aluminium cell is its "valve action", which enables an electric current to pass from the electrolyte to the aluminium electrode, but prevents its passage in the opposite direction. In this discussion, the direction in which the current proceeds to the aluminium from the electrolyte will for convenience be designated as "positive". It has been found that as soon as a "negative" current begins to flow, the aluminium becomes covered with a thin oxide film overlaid by a thin gas film. The resistance of these films, especially the latter, is very high; moreover, since the films are so thin, the cell acts as a condenser in the direction of "negative" current. For "positive current" the gas film breaks up, although the oxide film remains on the plate, its duration depending on the use to which the cell is put. (This oxide film is however probably punctured over its entire surface, to afford a passage for the current.)

Prof. Schulze, who made experiments on aluminium condensers in the Reichsanstalt,* found that the oxide film really serves as a foundation for the gas film, and remains on the plate indefinitely. Fig. 1 shows a hypothetical diagram of a cell having one aluminium electrode and one lead electrode. The latter cell, (Fig. 2,) has two aluminium electrodes, and acts as a condenser for either positive or negative, and hence for alternating, current.

*Electrochem. and Met. Ind. Vol. VII, P. 272.

Chemical Reactions.

Although there are many electrolytes which may be used, only two will be discussed in this paper, as they are fairly typical, and each has particular advantages and disadvantages.
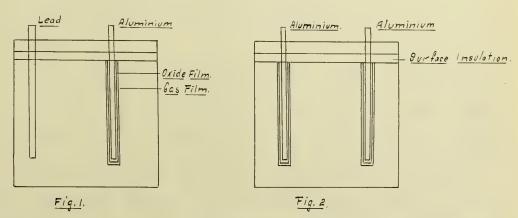
Sodium bicarbonate, $NaHCO_3$, being cheap, is sometimes used in certain kinds of cells. There are two principal reactions, which will be called primary and secondary. The primary breaks up the bicarbonate, forming sodium hydroxide:

$$Na\ H\ CO_3 + H_2O = Na\ O\ H + CO_2 + H_2O.$$

(This is the principal reaction, and apparently provides the gas film.) The secondary reaction attacks the aluminium and does not aid the rectifying property:
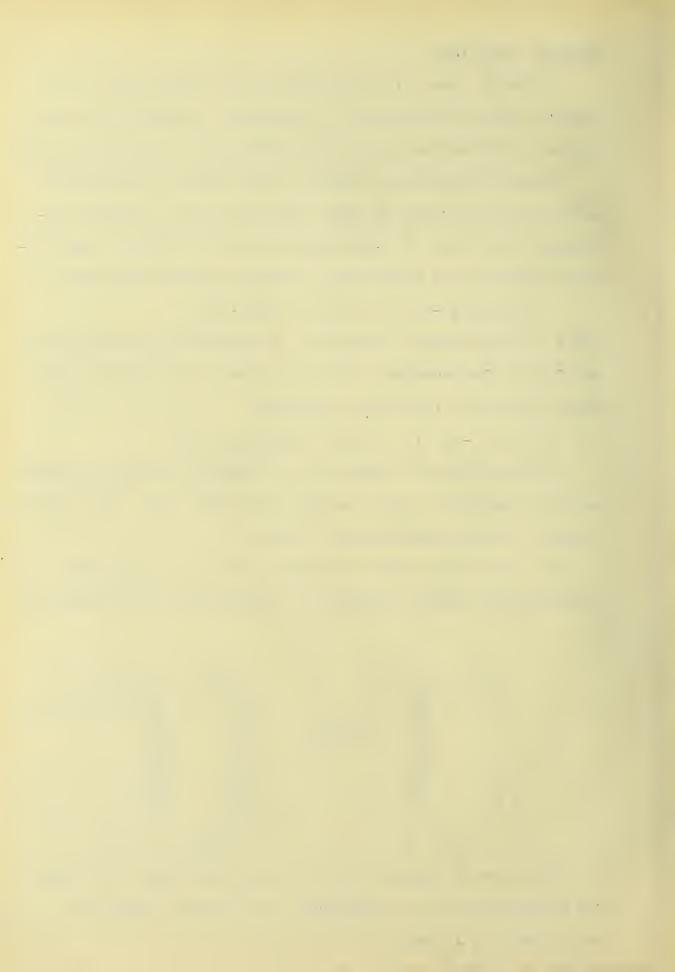
$$2\ Na\ O\ H + 2\ Al + 2\ H_2O = Al_2Na_2O_4 + 6H.$$

This destructive action can be partly prevented by changing the electrolyte and by keeping the cell cool, since boiling alkalies attack aluminium very readily.

In a cell using this compound, 0.322 g. of aluminium is destroyed per gram of bicarbonate decomposed. Since aluminium

Fig. 1.　　　　Fig. 2.

is comparatively expensive, it is necessary either to prevent the destruction of the electrode, or to use an electrolyte which does not attack it.

Ammonium salts have been used extensively for all types of cells, both rectifying and condensing. The results obtained herein are for ammonium carbonate and the sodium compound above mentioned. The results were very satisfactory. With the ammonium carbonate, the primary reaction is

$$(NH_4)_2 CO_3 + H_2O = 2NH_4OH + CO_2.$$

The secondary reaction is similar to that where sodium salts are used, except that the attack on the aluminium is apparently much slower. Moreover, the ammonium hydroxide which is formed decomposes at the higher temperatures, into NH_3 and H_2O, thus preventing further attack on the electrode. A small quantity of ammonium aluminate is, nevertheless, formed.

The Anode.

In "one electrode" cells, (having only one aluminium plate,) the anode is made of some material whose contact resistance with the electrolyte is small, and which will not react chemically with any substance in the cell. Iron and lead are the most common metals for anodes, and carbon may be used equally well. Tests made with these three substances show little difference in the performance of the cell.

The Electrolyte.

Freedom from impurities is the prime requisite of the electrolyte. Tests show that the presence of very small quantities of metallic salts diminish and in some cases destroy entirely the rectifying action. The concentration of the electrolyte does not affect this property appreciably, but determines to a certain extent the I^2R loss, so that for most purposes it is desirable to use a saturated solution, thus saving

power and insuring uniform results.

Tests described in the following chapter tend to show that the electrolyte should be kept in motion, where the current density in the cell is high. Movement of the electrolyte is necessary for two reasons: that fresh solution may be in contact with the aluminium at all times, and that the heat may be carried away.
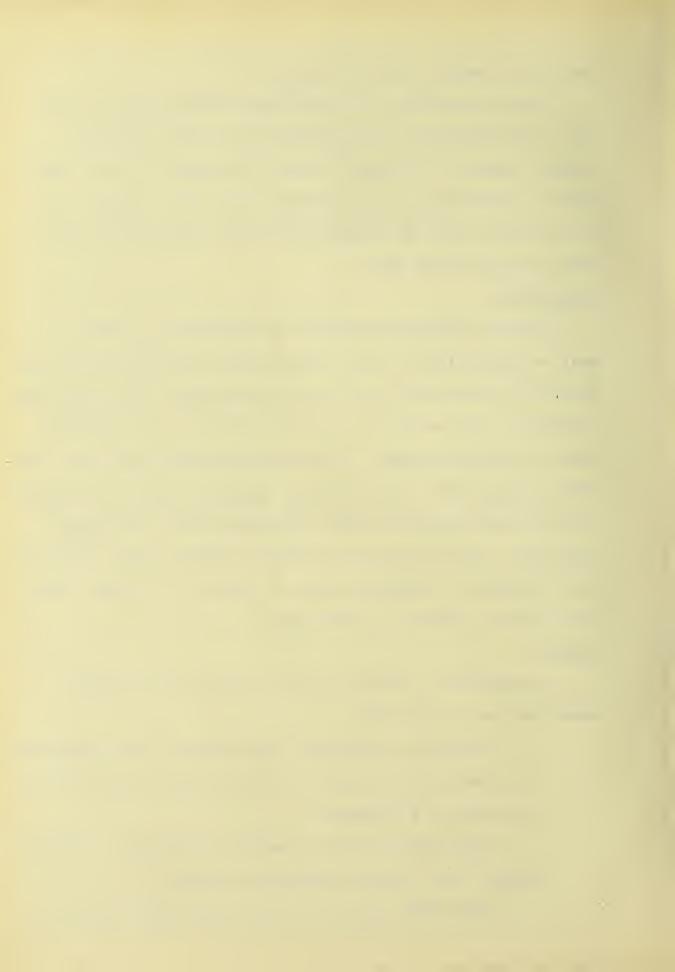
The kathode.

When an aluminium electrode is inserted in a cell, it must be perfectly free from grease, dirt, and any oxide film formed by contact with the air. The insulating film will then be uniform and continuous. For best results, the electrode must be chemically pure, as the cheaper grades which are sometimes alloyed with zinc and other substances are not suitable. In all tests described herein, chemically pure electrodes were used, and these were thoroughly cleaned before the cells were assembled. Alcohol was used to remove the grease, and the oxide was removed by polishing.

Summary.

The essential features of the aluminium cell may be summarized in a few words:

1. Current is prevented from passing from electrolyte to aluminium by a gas film, which also acts as the dielectric of a condenser.

2. Destruction of the aluminium exists to a certain extent, and is not a desirable feature.

3. Rectifying action for small voltages is indepen-

dent of the degree of concentration of the electrolyte.

     4. Freedom from impurities, moderate current densities, and low temperatures are necessary.
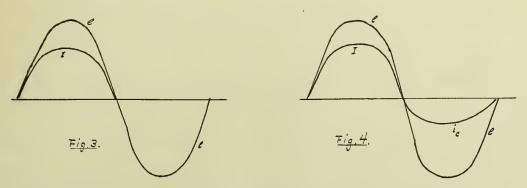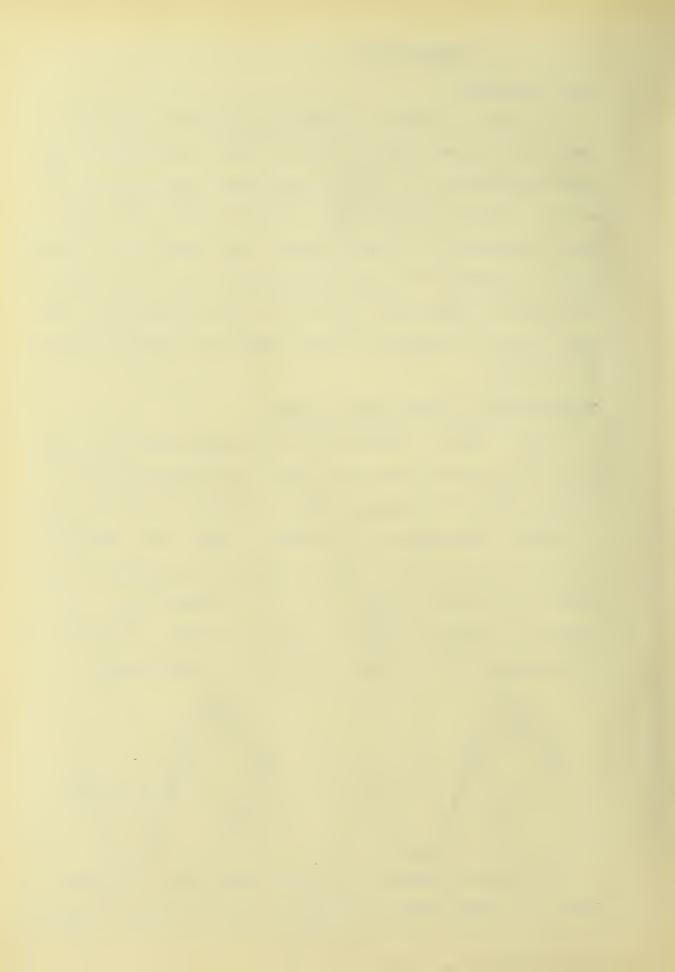
CHAPTER TWO.

Test apparatus.

In order to secure uniformity of results, the cells used for tests were made in cups of 225 c.c. capacity. The aluminium surface in the electrolyte was approximately 13 sq. cm. and that of the anode, 25 sq. cm. The cells were partly immersed in a tank of water, the temperature of which could be regulated to suit requirements. Cells were made up in groups of five each, the cells of each group being identical. Thus, an average of five results for every condition was obtained.

Determination of Rectifying Action.

Fig. 3 shows approximately the current wave in a "one way cell, when an alternating E.M.F. is impressed upon it. For one cycle, the average value of current for such a wave is 0.3175, the maximum being taken as unity. The effective value of the wave is 0.5, and the ratio of average to effective is therefore 0.635. If an A. C. ammeter and a D. C. ammeter be placed in series on such a circuit, the ratio of the readings will be 0.635, for perfect rectification.

Fig. 3.   Fig. 4.

The ratio, however, is always less than 0.635 since there is a small amount of charging current in the "negative"
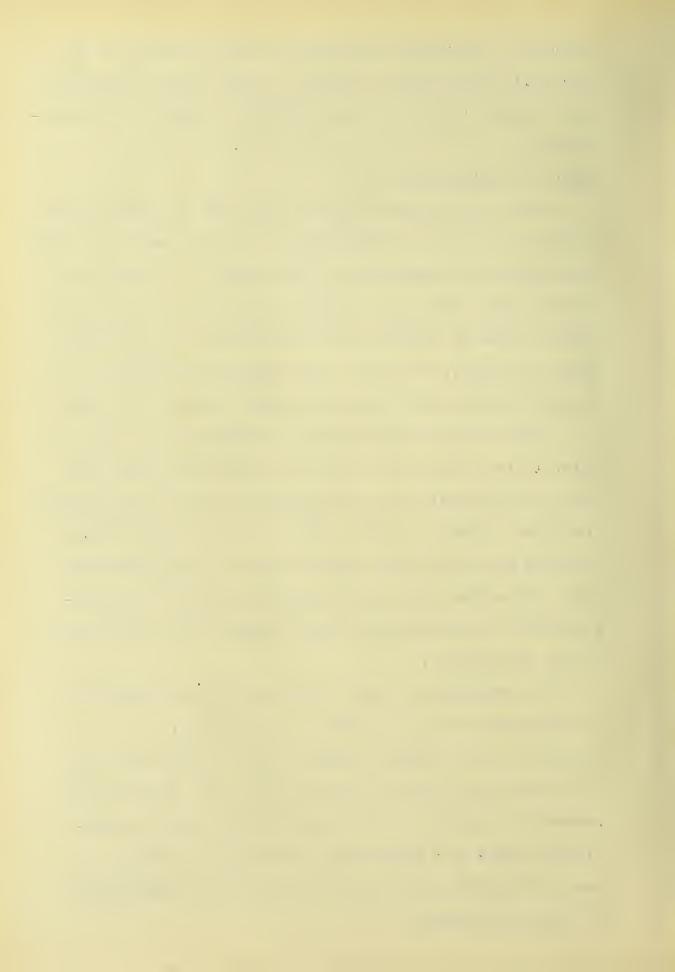
direction. The amount of charging current depends on the
dielectric area and the voltage, as with other condensers.
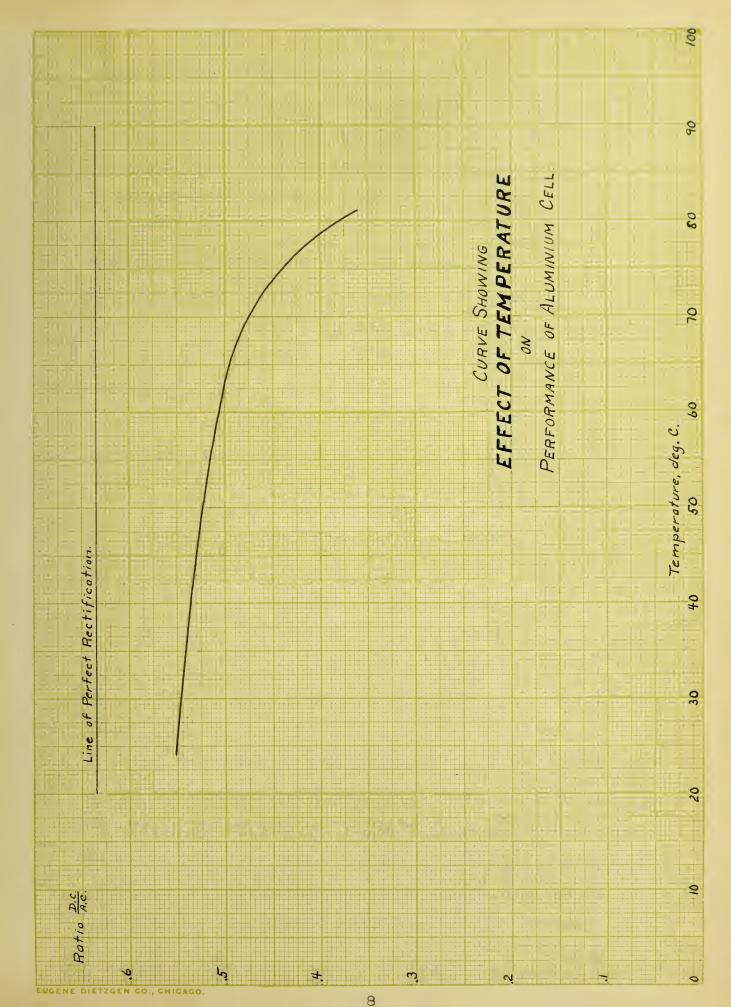The charging current is shown in Fig. 4, where it is denot-
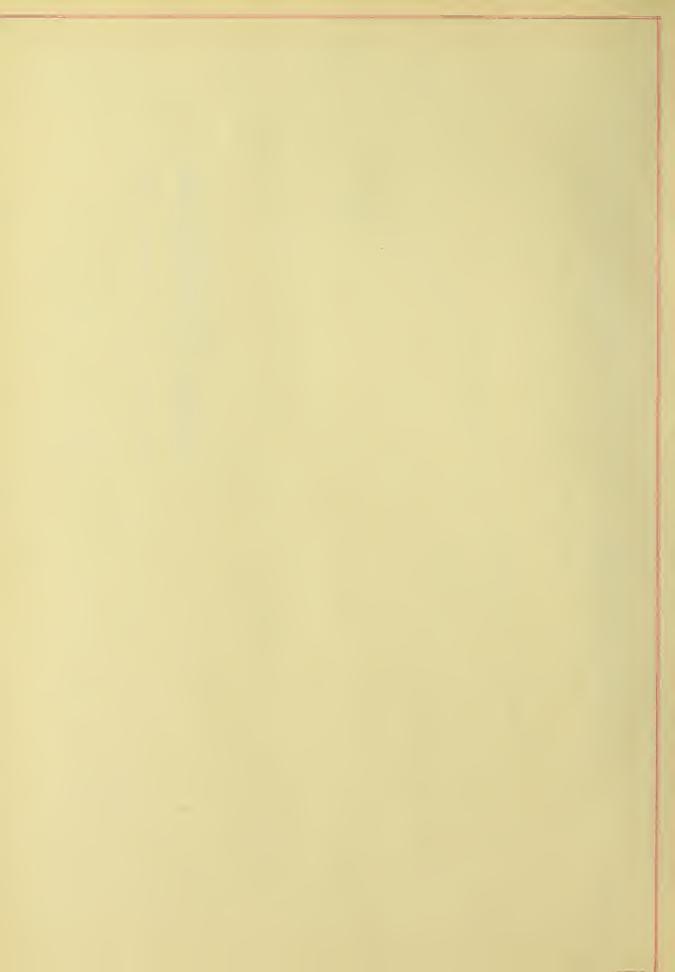ed by i_c.

Effect of temperature.

Since the rectifying action of a cell is greatly dim-
inished by a rise in temperature, it is interesting to know
the relation of temperature to the amount of current rec-
tified. Tests were made for this purpose, and curves were
plotted from the results. The one shown on the following
page is the mean of nearly four hundred observations, and
in very few cases did the points fall far from the curve.

Since the rectifying action is dependent on the gas
film, it is evident that the high temperatures cause the
gas to rise rapidly from the aluminium plate, thus allowing
"negative" current to flow. That the kind of electrolyte
does not alter the shape and position of the temperature
curve shows that the high temperature affects the recti-
fication by destroying the film, instead of by any action
on the electrolyte.

The temperature curve is plotted from observations
on thirty five cells of various construction. It is
believed to be tolerably accurate for a large variation
in the kind and quantity of materials used. The distance
between an asymtote to the curve and the perfect recti-
fication line is a measure of the charging current. For
larger electrodes and higher voltages the distance would
of course be greater.

CURVE SHOWING
EFFECT OF TEMPERATURE
ON
PERFORMANCE OF ALUMINIUM CELL.

Temperature, deg. C.

Line of Perfect Rectification.

Ratio $\frac{D.C.}{A.C.}$

EUGENE DIETZGEN CO., CHICAGO.

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Concentration of Electrolyte.

As stated in chapter one, the degree of concentration of electrolyte determines the I^2R loss only. The resistance of electrolytes of various degrees of concentration has been determined, and the internal losses checked thereby. (A saturated solution is of course the lower limit of specific resistance under normal conditions.)

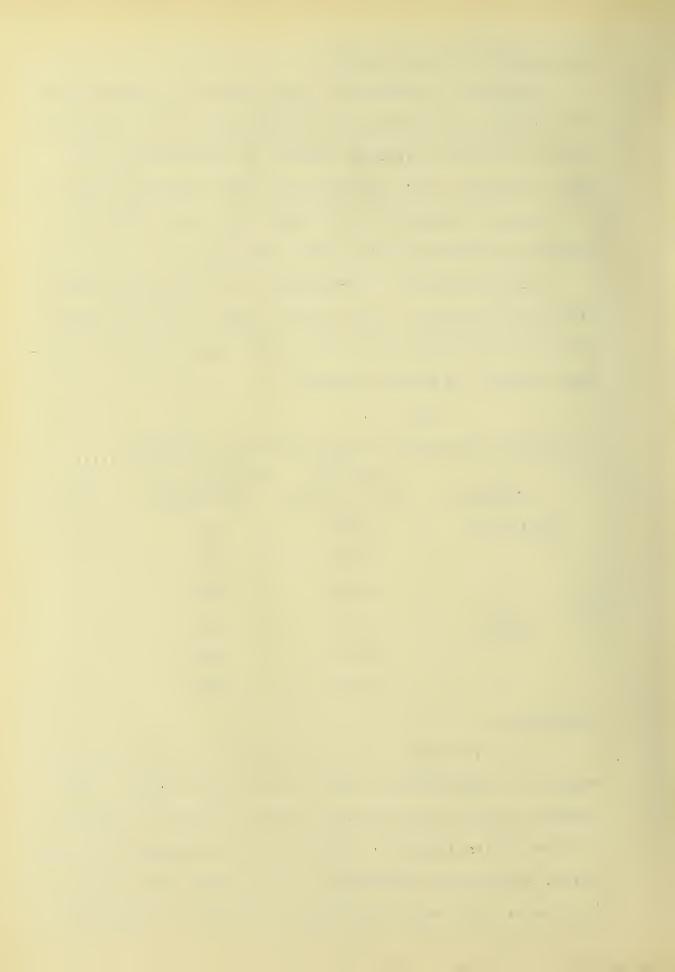For measurements of resistance, the electrolyte was placed in a porcelain tube having carbon terminal blocks. The contact resistance with the carbon was neglected on ac-count of the low current density.

Table I.

Specific Resistance of Electrolyte at 20° Cent.

Substance.	Ratio of Salt to Water.	Resistance per cm^3, ohms.
$(NH_4)_2CO_3$	.156	40.3
"	.077	52.2
"	.040	96.0
$NaHCO_3$	.172	54.6
"	.069	72.7
"	.036	127.2

Impurities.

For good results it is necessary to use pure water in making the electrolyte. Traces of iron and metallic salts commonly found in hard water greatly increase the leakage. To demonstrate this fact, the test of a condenser is given below, showing the difference in the losses when using im-pure water. The test data shows that even at a higher tem-

perature the losses when using pure water are 33% less than
with water containing a small quantity of iron.

Table   II.

Effect of Impurities on Condenser Losses.

Volts	Amperes	Watts	Kind of Water	Temp.deg.C.	Power Factor
220	0.1	6	Tap Water	19	.273
220	0.1	4	Distilled	23.5	.182

Dirt in the bottom of a cell will cause leakage, and
often complete breakdown, at the higher voltages. The dirt
touching the electrodes prevents the formation of a film
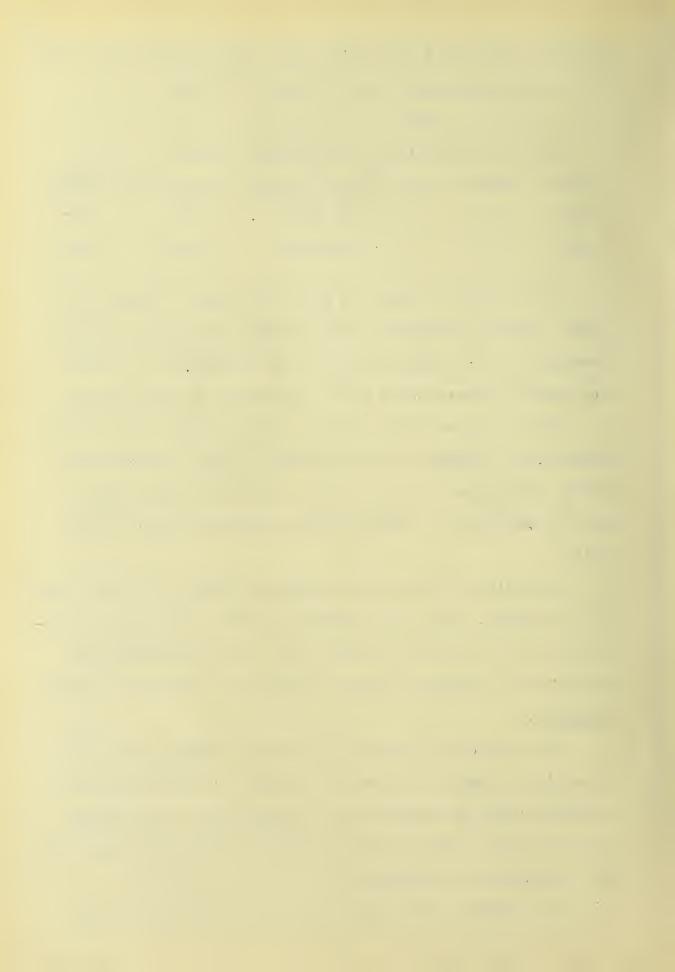and hence becomes merely a low resistance in the circuit.

Dirty electrodes may either cause leakage, or, if non-
conducting, decrease the active area. Since aluminium ox-
idizes if exposed to the air for a time, new electrodes
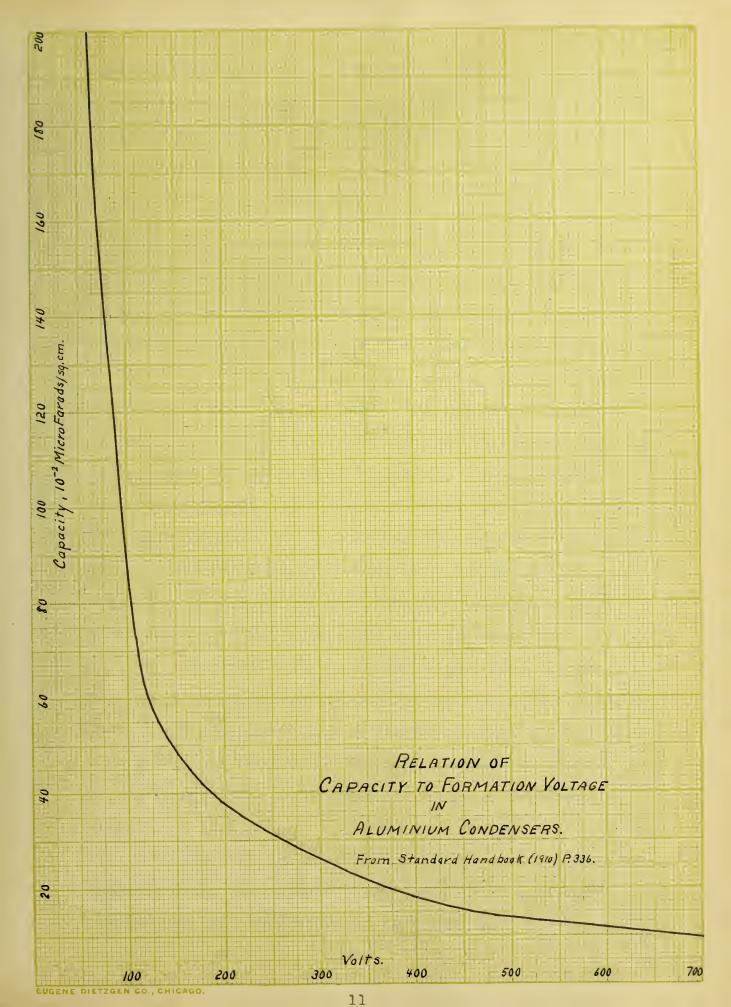must be polished or scraped before inserting them in the
cell.

Aluminium is sometimes alloyed with zinc, in which case
it is useless, since the insulating film is defective where-
ever there is a trace of other metal than aluminium. This
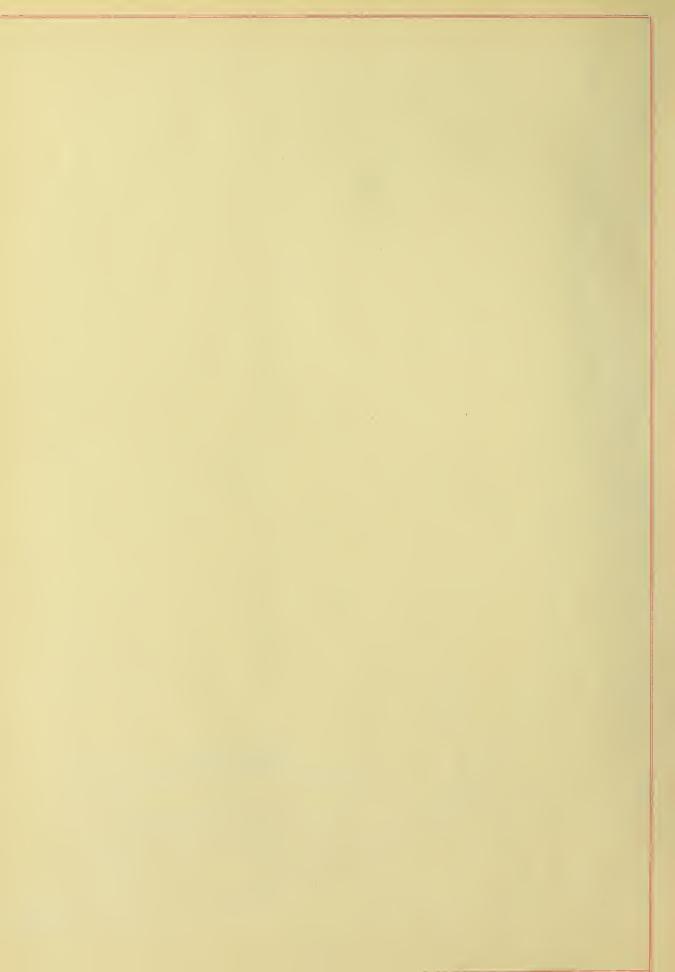fact forms a frequent source of trouble in commercial cells.

Capacity.

"The capacity", says Dr. Schulze, "depends only on the
formation voltage". A curve is included in this paper, con-
structed from the results of his experiments, which show
this relation. Lack of space prevents further discussion of
the variation of capacity.

The capacity of a double electrode cell may be calcu-

Capacity, 10^{-2} MicroFarads/sq.cm.

Volts.

RELATION OF
CAPACITY TO FORMATION VOLTAGE
IN
ALUMINIUM CONDENSERS.

From Standard Handbook (1910) P.336.

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lated in the same manner as a dry condenser in parallel with a resistance. For example in the second condenser tabulated in Table II, the IX drop is 216 volts;

$$X = 2160 \text{ ohms};$$

$$C = \frac{1}{2\pi fX} = 1.25 \text{ M.F.}$$

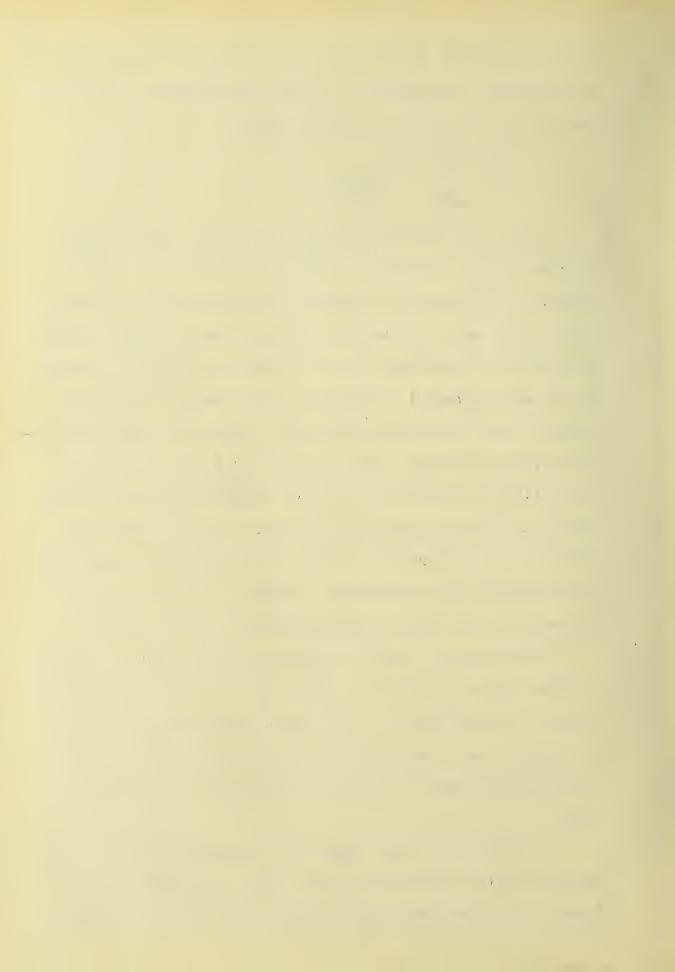For a one electrode or "one way" cell, however, the problem is very different. There are two simple methods: First, if the amount of leakage is negligible, the charging current may be calculated from the ammeter ratio, and the capacity determined from the charging current. Second, if an oscillograph is available, the amount of charging current can be determined from the current wave and the capacity found. The more exact method would be to consider the cell as a parallel circuit of capacity and resistance, each path having a single pole switch, and the switches being opened alternately in step with the alternations of the current. This calculation, however, is rather complicated, and is not within the scope of this paper.

The principal thing to remember regarding the capacity is, that after a voltage is applied to a cell, the capacity becomes a fixed quantity, its value depending on the value of voltage, and remains practically constant as long as the working voltage is below the voltage of formation.

Life.

The life of a cell depends on so many factors that no specific data is available which would cover all cases. However, if the temperature is kept low, the life depends

chiefly on two things: the decomposition of the electro-
lyte, and the destruction of the aluminium. Since the al-
uminium electrode is usually quite large, its life for low
temperatures greatly exceeds that of the electrolyte, and
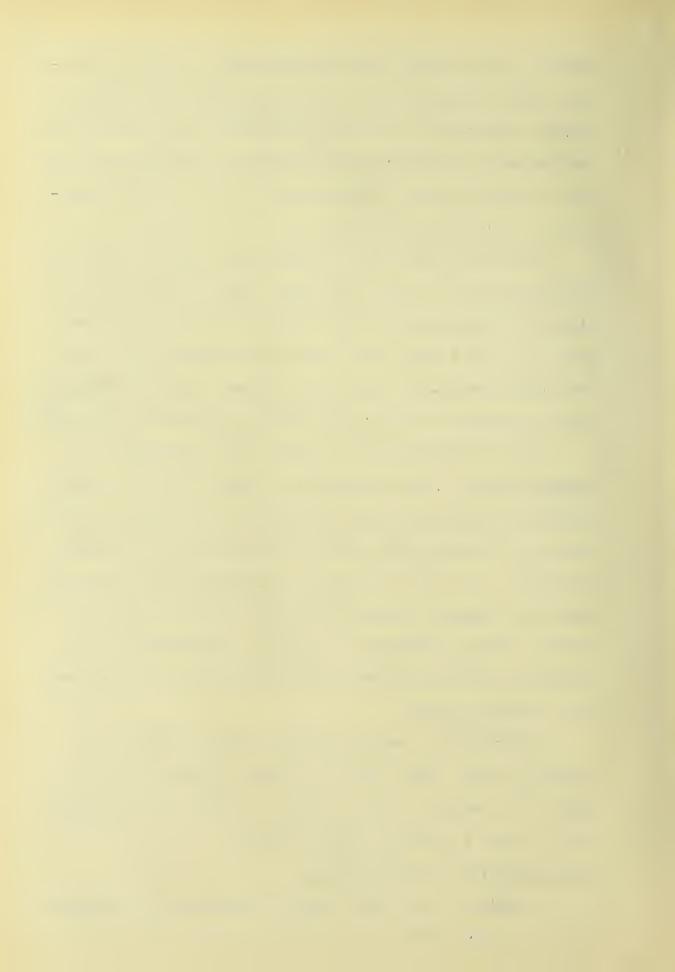the life may be said to depend only on the kind and quan-
tity of electrolyte used.

For cells having 225 c.c. capacity, the life for low
density current is about 120 hours, with a saturated sol-
ution. In tests made to establish this figure, a current
density of 0.04 ampere per sq.cm. of aluminium was used.
For higher densities, the life is proportionately shorter.
For intermittent service, the life is enormously increased.

When the electrolyte is nearly all decomposed, the
leakage current rises gradually in value. It is therefore
difficult to determine at what point rectification stops
entirely. For most work, such as the charging of storage
batteries, it is not desirable to operate beyond the point
where the leakage exceeds 10% of the rectified portion of the
current. Where condensers are used, a breakdown of the
insulating films is shown by the heating of the cell, and
by a crackling noise.

Rectification ceases entirely if the solution is
allowed to boil. The life of a large cell may thus be
abruptly terminated unless watched closely. It is impor-
tant to have a reliable cooling device.

Characteristics of single cells.

In order to show the relative performance of various
types of single cells, the following table has been pre-

pared from the results of tests.

Table III.

Performance of single, or "one way" cells.

Volts	Amp.	Watts	Electro- lyte.	Anode	Temp. Cent.	Power Factor.	Ratio, DC:AC
13.6	1.61	19.2	Sod.Bic.	Lead	24	.875	.404
15.	1.61	20.8	"	"	"	.86	.433
13.8	1.42	17.3	"	"	"	.887	.282
17.2	1.60	18.0	Amm.Car.	"	"	.654	.562
18.0	1.43	16.0	"	Iron	"	.622	.593
14.7	1.42	17.3	Sod.Bic.	"	"	.833	.350
13.1	1.40	16.2	"	C.	"	.880	.313

The results are for cells which had been operated for several hours, and are representative of this type of cell. It is evident that the ammonium carbonate gives the better results from the standpoint of rectification.
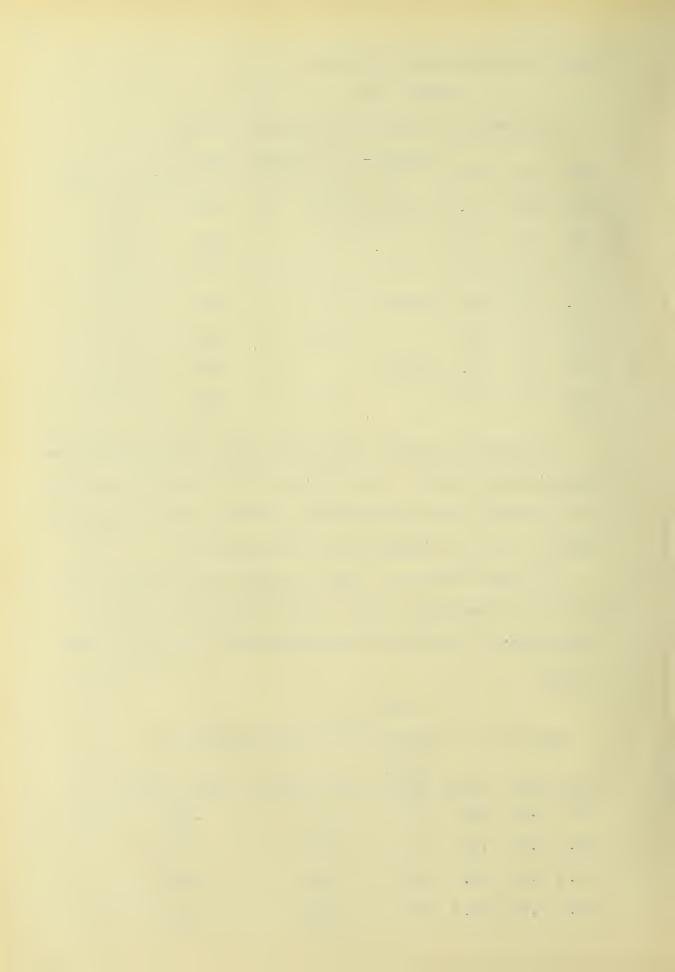
The power factor of single cells under various conditions of temperature and voltage varies considerably. Tables 3 and 4 show the variations under two sets of conditions.

Table IV.

Variation of Power Factor with Temperature.

Volts	Amps.	Watts	Temp. deg.C.	Power Factor	Ratio DC:AC
15	1.61	20.8	24.	.86	.433
12.3	1.54	16.8	50.	.887	.195
13.4	1.56	17.8	60.	.853	.160
13.4	1.59	18.4	66.	.863	.138

Results obtained in Table 4 are for a lead anode, and
a solution of sodium bicarbonate. The variation of power
factor probably depends on several conditions which are
changing as a result of the temperature rise. For this
reason, the change does not seem to follow any particular
line. The decrease in the rectifying action is, however,
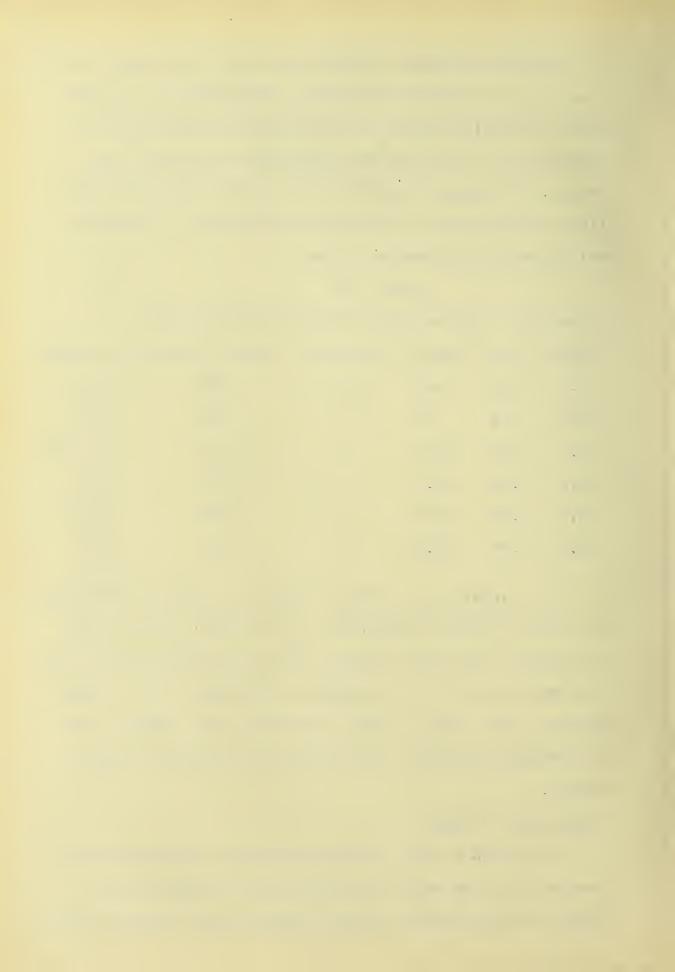well shown by the ammeter ratio.

Table V.

Variation of Power Factor with Current Density.

Volts	Amps.	Watts	Temp.deg.C.	Ratio, DC:AC	Power Factor
8.8	.55	4.2	24	.365	.868
10.4	.84	7.6	"	.238	.871
11.9	1.00	10.2	"	.200	.856 (?)
12.6	1.22	13.6	"	.229	.885
13.5	1.43	17.7	"	.244	.913
14.5	1.67	22.4	"	.257	.923

The variation of current density is really a variation
of volts per cell. Therefore it is seen that with a rise
of voltage and current density the power factor rises. This
fact applies also to an aluminium condenser, and in either
apparatus the energy current increases more rapidly than
the charging current, thus causing an increase in power
factor.

Protection of Anode.

As stated in the preceding chapter, some electrolytes
destroy the aluminium, and hence must be changed often
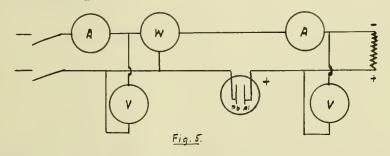where the cell carries current continuously. Another source

of trouble is the burning of the aluminium at the surface
of the electrolyte, caused by the current jumping across
the infinitesimal distance between air and liquid. This
difficulty is obviated either by insulating the aluminium
at the surface with wax or rubber, or by covering the cell
with oil. The latter method is the easier, and was used
in the tests for this investigation, with good results. It
is also used in commercial work, and has the additional
advantage of hindering evaporation.

The Single Electrode Rectifier.

A cell with one electrode of aluminium and one of some
other metal, such as lead, constitutes a simple rectifying
device, which if connected in an A.C. circuit will deliver
an almost unidirectional current. The negative lobe of the
A.C. wave will be nearly obliterated, only a small amount
remaining as charging current and leakage. The connections
are as shown in Fig. 5, and include the instrument con-
nections for testing.

Fig. 5.

The efficiency of the cell, unless of special design,
is very low, and except in cases where the amount of direct
current required is small, it is not recommended. By a
study of the causes of loss in the rectifier the conditions
might be improved, but it is doubtful whether the efficiency
could be made much better than is indicated in the follow-
ing test data.

Table 6 gives the results of a test on the single elec-
trode cell as a rectifier; No. 1, using $NaHCO_3$ electro-
lyte, and No. 2, using $(NH_4)_2CO_3$. It is interesting to note
the large leading current, which in rectifiers of large
capacity might be used to improve the power factor of a
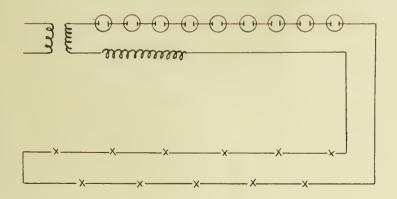distribution system. The efficiency, however, is too low

Fig. 6A. Constant Current Rectifier, (high voltage).
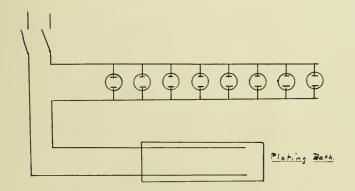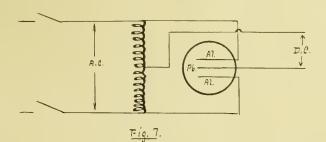

Plating Bath.

Fig. 6B. Constant Voltage Rectifier.

(Proposed Schemes for Rectification on a Large

Scale).

Fig. 7 gives the wiring diagram for the double electrode rectifier, without test connections. The circuits are identical with those of the mercury arc rectifier, and need no explanation.

Table 7 gives the results of a test of a double electrode cell, of the same size as the single cell, but con-

Fig. 7.

taining an additional aluminium plate. Ammonium carbonate electrolyte was used, and the poor regulation given by this substance is again in evidence. The table shows very good power factors, and these are probably caused by the balance between the inductive reactance across the line and the capacity reactance of the cell itself.

Table   VII.

Test of a 6" x 8" Double Electrode Rectifying Cell.

AC Volts	AC Amps.	AC Watts	Temp.	DC Volts	DC Amps.	Eff.%	P.F.%
112.5	1.2	135	26.	11.5	2.25	18.7	100
109.0	1.6	175	28.5	7.0	3.15	12.6	100
109.0	2.0	215	29.	5.0	3.35	8.95	99
108.5	2.5	260	30.	4.25	4.75	7.77	96

Another double electrode rectifier was tested; sodium bicarbonate was used, and the cell contained 225 c.c. of electrolyte. Table 8 gives the results of this test.
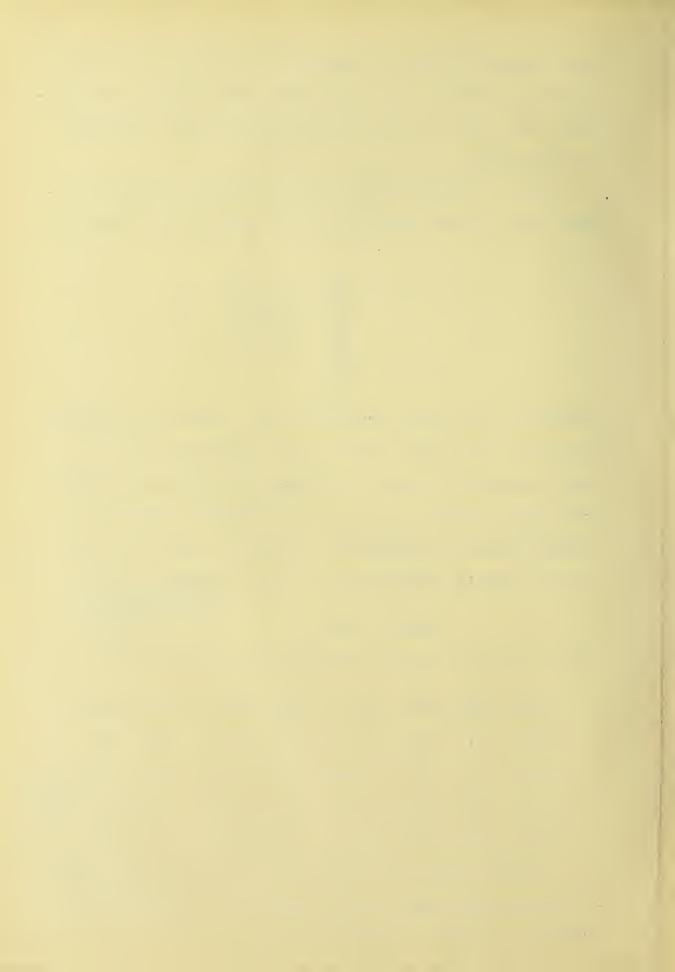
Table VIII.

Test of a Small Double Electrode Rectifying Cell.

AC Volts	AC Amps.	AC Watts	Temp.	DC Volts	DC Amps.	Eff.%	P.F.%
112.0	-	35	35	-	0	0	-
112.0	-	62	36	41.5	0.5	32.5	-
110.5	.75	83	37	39.5	1.0	47.6	100
110.5	.90	105	38	40.	1.25	47.6	100
109.0	3.50	390	38	32.	6.4	52.5	100

The data shows that a smaller cell than the 6" x 8" size is suitable for values of power under 500 watts. The efficiencies for the small cell are much greater, and the power factor is unity for practically all loads. The no-load loss is comparatively low.

The above rectifiers, while of no value commercially, point out the logical conclusion on which the design of all other rectifiers of this type must be based; i.e., that that portion of the cell in which the rectification takes place should be as small as possible, and should be insulated from the receptacle in which the reserve portion of the electrolyte is kept. Furthermore, the rectifier must be kept at a temperature between 25° and 35°, Cent., by a suitable cooling device, because for temperatures above 35° the leakage has been shown to be excessive, while cold electrolyte has a comparatively high resistance, which is undesirable.

Electrolytic Lightning Arresters.

When lightning on a high tension line discharges over

the gap of an arrester, there is a tendency for a power
arc to be established, supplied by energy from the line.
To prevent this, a high impedance is put in series with
the spark gap on systems of moderate potential, but on
systems of 15000 volts and higher, any device giving suf-
ficient protection from power arcs will offer too much
impedance to the lightning discharge. A device which
would break down under a severe static stress, and instant-
ly offer high impedance to the consequent power arc, would
be the ideal protective device, and is found to a certain
extent in the now familiar electrolytic arrester.

The device consists essentially of a number of double
electrode cells in series, the breakdown voltage of the
set exceeding the normal line voltage. A set of cells
is connected between each line and the ground, or in a
similar manner. The high potential of the static dis-
charge breaks down the insulating films, but these are
immediately restored when the discharge has passed, and
effectually prevent the formation of a destructive arc.

The electrolyte used in the commercial arresters is
changed by the manufacturers, and its exact composition
is kept secret. However, knowing from the experiments in
chapter two that only certain substances may be used, and
that these must be pure salts of one metal, it is not
difficult to find an electrolyte which will give good
results in an arrester. In commercial work the saturated
solutions are used in winter on account of their low
freezing point. The degree of concentration depends on

the climate where the arrester is to be used and on the thickness of the film desired.

Since the energy loss is considerable when the arrester is across the high potential line, it is connected in series with a spark gap, so that charging current will not flow continually. In order to maintain the film at the proper thickness, the spark gaps are closed for a few seconds, at intervals of from one to fourteen days, depending on the kind of electrolyte used.

Condensers on Distribution Systems.

It has been proposed to operate aluminium condensers on systems having a large lagging current, in order to raise the power factor, but there is no record of such a system in use at present. The chief objection is the large loss which usually exists. If the loss could be kept within reasonable proportions, the aluminium condenser would doubtless replace many synchronous condensers now in use.
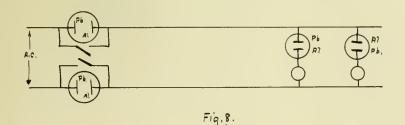
Rectifiers for Emergency Service.

A test was made by the writer during the preparation of this paper, to determine the practicability of securing large overload currents from the rectifier for a short time. With this in view, several large cells were assembled, and power amounting to several kilowatts per gallon of solution rectified. One way in which the rectified current was utilized was in starting a rotary converter from the D.C. side, this plan being entirely successful. It would be practicable to build a rectifier at moderate cost, (about 50 cents per

kilowatt for 100 Kw. rotaries, and 25 cents for larger

sizes,) which would start a rotary without difficulty.

Either the single or double electrode type might be used,

although the latter is preferable.

Selective Signalling.

Fig. 8 shows a simple application of the one way cell

to selective signalling. With the arrangement shown, three

Fig.8.

distinct signals can be made on two wires. For example,

with switch 1 closed, lamp 2 will burn; with switch 2 closed

lamp 1 will burn; and with both switches closed, both lamps

will burn. By certain connections, using condensers and

one way cells, this system may be extended until the number

of different combinations of burning lamps far exceeds

the number of conductors used.

Aluminium cells in telephone work.

The signalling device just described may be used on

4-party telephone lines for selective ringing. Aluminium

cells may also be used on central energy telephones, as

condensers across the line in series with the bell, as

electrolytic condensers would be cheaper than dry types,

and on such intermittent service would have long life.

Lightning discharges would not ruin electrolytic condensers

used in connection with outdoor lines, as might be the